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RESEARCH MEMORANDUM

IGNITION OF AMMONIA AND MIXED OXIDES OF NITROGEN IN 200-POUND-THRUST ROCKET ENGINES AT 160° F

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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SUMMARY

A study of the ignition of ammonia and mixed oxides of nitrogen at 160° F was made with and without fuel additives utilizing small-scale rocket engines of approximately 200 pounds thrust. All experiments were conducted at sea-level pressures except two at pressure altitudes of 61,700 and 84,300 feet. Each experiment at sea-level pressure resulted in a start which attained full chamber pressure and which was followed by stable combustion. Successful ignitions but unsatisfactory starts were obtained at subatmospheric pressures. Fuel-line additives were useful aids in engine starting; lithium was more effective than calcium.

INTRODUCTION

The propellant combination of liquid ammonia and mixed oxides of nitrogen is attractive primarily because of its thermal stability and its compatibility with ordinary materials of construction (ref. 1). Because of its nonhypergolic nature at and below room temperature, an experimental investigation was conducted to determine the type and amount of fuel additive necessary to produce ignition and sustained combustion (ref. 1). It was found that small amounts of lithium or calcium inserted in the ammonia flow line induced satisfactory rocket-engine starts from room temperature to -85° F.

Although these experiments yielded means for starting rocket engines in the indicated temperature range at sea-level pressure, the feasibility of producing similar results at higher temperatures and subatmospheric pressures by the same methods remained unknown. In order to determine whether the results of reference 1 were applicable to other conditions, the investigation was extended to include experiments with 200-pound-thrust engines at 160° F and pressure altitudes to 84,300 feet, and the results are reported herein.

APPARATUS AND PROCEDURE

The apparatus consisted of small-scale rocket engines of approximately 200-pounds thrust, propellant valves and tanks, a catalyst receptacle in the fuel flow line, a gas pressure-supply reservoir, means for obtaining desired temperature and initial ambient pressure conditions, and instrumentation for indicating and recording combustion-chamber pressure and other operating variables. Except for a few modifications, the entire system was essentially the same as the low-temperature test facility described in reference 1 and is shown, with the changes, in figure 1. 3184

Two engines were used in this investigation. They differed only in length, having characteristic lengths L^* of approximately 50 and 25 inches. The larger one was used for all experiments at sea-level pressure. The smaller one was employed in only two runs, each at subatmospheric pressure. Both had stainless-steel injector heads and spun aluminum chambers and nozzles. A schematic diagram of the engines is shown in figure 2.

In order to provide the required high ambient temperature of 160° F, the entire engine assembly and propellant tanks were immersed in a water bath containing five 1500-watt electric resistance heaters. To prevent engine burnouts during operation, a portion of the water was pumped at high velocity through a close-fitting shroud surrounding the nozzle.

Means for simulating subatmospheric pressures used in some of the experiments included a 1500-cubic-foot altitude tank, a large vacuum pump, and other auxiliary equipment. The system is described in detail in reference 2.

Catalyst addition to the fuel line, propellant-tank loading, and engine operation were all similar to the corresponding procedures outlined in reference 1.

Runs were conducted with and without catalysts. When a catalyst was used, approximately 1 gram was placed in the ammonia-line receptacle (fig. 3) prior to each propellant loading, which consisted of 3 to 5 pounds of fuel and 4 to 7 pounds of oxidant. The propellant charge was usually sufficient for two to six runs. Presence of small amounts of catalyst after exhaustion of the propellant supply indicated an excess at all times. Because of this operating procedure, the amount of catalyst consumed during each run was indeterminate. After each series of runs with a particular catalyst, the entire propellant flow system including the engine was cleaned and dried by the consecutive use of either water, denatured alcohol, and helium (lithium series) or dilute nitric acid, water, acetone, and helium (calcium series).

In each run, the time for full valve opening was about 0.2 second. Full propellant flow was obtained at about 3/4 full valve opening. Time intervals from the beginning of injection-pressure rise to steady-state conditions of propellant flow and combustion-chamber pressure were of the same order of magnitude as those reported in reference 1 (0.3 to 1.0 sec). Propellant injection pressures were all approximately 500 pounds per square inch gage.

The response rate of the entire chamber-pressure recording system was determined experimentally. The imposition of a step change upon the system yielded 63.4 percent of the maximum value in approximately 0.025 second.

PROPELLANTS

The fuel used in all the experiments was refrigeration-grade anhydrous ammonia which conformed to Federal Specification O-A-445. The fuel additives were lithium and calcium and were treated as described in reference 1. The oxidant, "mixed oxides of nitrogen," was a mixture of NO and NO_2 with the composition 26.7 weight percent nitric oxide and 73.3 weight percent nitrogen dioxide.

RESULTS

Lithium as Catalyst

Sixteen runs were conducted with the 50 inch L^* engine at approximately 160° F and sea-level pressure using lithium as the ignition catalyst. The calculated oxidant-fuel weight ratios O/F varied from 1.9 to 3.0. A summary of the ignition data is shown in table I. A plot of combustion-chamber pressure as a function of time measured from the beginning of propellant flow through the propellant valves is presented for each run in figure 4. (The values of pressure for run 221 are not absolute because of the superimposition of a small, variable instrument zero-shift.) Except for two runs in which sharp pressure transients of short duration occurred, a smooth engine start followed by stable combustion was obtained in each test.

In general, the rise of chamber pressure to its peak equilibrium value was not continuous, but included a point of inflection beyond which the pressure increased very rapidly to a value near its maximum (fig. 4). Although this pattern occurred in every case, it was more clearly defined in some runs than in orders (e.g., runs 222 and 227). The chamber pressure course of a typical run may be described in detail by the following chronological series of events. From the moment that the propellant valves began to open until an initial pressure rise was indicated in the

chamber, there was a time interval of about 50 milliseconds. This delay period was due to three factors: (1) the flow of propellants from the valves, through the injector, and into the chamber, (2) the ignition delay of the propellant combination, and (3) the delay in instrument response. After beginning at a rate of approximately 2000 pounds per square inch per second, the pressure increased at a decreasing rate until it leveled off at about 200 pounds per square inch gage approximately 250 milliseconds after the start of propellant flow. After a period of time at this level ranging from <10 to about 60 milliseconds, the pressure usually rose at a very rapid rate (as much as 4500 psi/sec) and 3184
then leveled off again at some value that either remained constant or changed slightly as the components of the propellant feed system approached equilibrium. Combustion-chamber pressures near equilibrium values were reached 300 to 400 milliseconds after initial movement of the propellant valves, and ranged from about 220 to 370 pounds per square inch gage.

In addition to this general pattern, two of the runs had sharp transient pressure pulses which occurred during the first pressure rise (100 to 150 millisec after valve opening) and which had a duration of about 20 milliseconds (runs 221 and 225). The magnitudes of these impulses are unknown because the rates of pressure rise were greater than the instrument response rate; therefore the peaks shown in figure 4 actually indicate minimal possible values. Indications of similar incipient reactions at about the same time were shown by some of the other runs.

Calcium as Catalyst

A series of eight runs was made with the 50 inch L^* engine at about 160° F and sea-level pressure using calcium as the catalyst. Oxidant-fuel ratios varied from 1.9 to 3.0. Results of these experiments are also shown in table I. Combustion-chamber pressure against time relations are shown for all runs in figure 5. As in the preceding series, each run was characterized by successful ignition and stable combustion.

In general, the chamber pressure-time curves produced by these runs differed from the lithium runs in that they were less reproducible and took longer to reach the final pressure value. Also, in contrast to the lithium series, there was no typical pattern that could be used to describe all the runs as a whole. There were some similarities, however, between the two sets of experiments. Most of the calcium-catalyzed runs, for example, also showed two discrete pressure rises before equilibrium was attained; in two of the runs, however, the first pressure rise appeared to be entirely absent (runs 237 and 238). As in the lithium series, the first pressure rise leveled off at about 150-200 pounds per square inch gage; in contrast, however, the duration of this plateau was as long as 700 to 900 milliseconds in some cases (runs 240 and 241). Chamber pressures near final equilibrium values were attained 300 to 1100 milliseconds after initial propellant-valve movement and ranged from about 250 to 350 pounds per square inch gage.

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Sharp transient pressure pulses encountered in the lithium series were also present in some of the calcium runs. In two instances, the sudden pressure rises occurred at the transition point between the two pressure plateaus (runs 240 and 241) and were of greater magnitude than impulses which occurred earlier in the ignition interval (e.g., run 239).

No Apparent Catalyst

At approximately 160° F, seven runs were conducted in which no catalyst was placed in the fuel-line receptacle; the flow lines had been chemically cleaned as mentioned previously. Oxidant-fuel ratios varied from 2.1 to 2.6. Results of these experiments are also included in table I. Combustion-chamber pressure - time relations are shown plotted in figures 6 and 7.

Five runs were made with the 50 inch L^* engine at sea-level pressure. As with all runs previously reported, no ignition difficulties were experienced. Engine starts reached full steady-state chamber pressures and the subsequent combustion reactions were stable.

The pressure-time curves resembled those of the calcium series and were just as erratic (fig. 6). The two-step pressure levels were clearly discernible in two of the runs (runs 244 and 246), but were masked by irregularities in the others. In runs 244 and 246, the first plateau began about 150 milliseconds after start of propellant flow and increased from 150 to 200 pounds per square inch gage over a period of 350 to 550 milliseconds. In each of these two runs, a sharp and very short transient pressure pulse occurred at the end of the first pressure plateau and appeared to initiate the subsequent pressure rise to the second and higher level. The other three runs (runs 243, 245, and 247) had similar pressure pulses of lesser magnitude. The final equilibrium pressures were about 350 pounds per square inch gage (except for run 247 in which it was never reached because of depletion of propellants) and were attained 500 to 800 milliseconds after initiation of propellant flow. The values of pressure are in the same range as those in the preceding two series.

Since all preceding runs in this project had yielded positive results, it was decided that more severe conditions of initial ambient pressure and chamber volume would be imposed in a few auxiliary tests with no added catalyst. Two more runs were made, each of which differed from all foregoing ones in two respects: (1) a 25 inch L^* engine was used, and (2) the pressure altitudes were 61,700 feet (run 249) and 84,300 feet (run 248). As with all other runs reported herein, no ignition difficulties were experienced; however, satisfactory engine starts were not obtained since the final equilibrium pressures never exceeded 150 pounds per square inch gage, a value which is considered too low for proper engine operation. Although the two discrete pressure levels shown by previous runs were also evident in these experiments, they were not very prominent in run 248 (fig. 7). In both runs, there were indications of the attainment of the first pressure plateau at <100 pounds per square inch gage.

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Since no catalyst was added to the system in any of the runs in this series and since certain light metals are successful catalysts, it appears that the ignition reaction may have been catalyzed by the aluminum engine and fittings in the fuel flow line. The possibility also exists that ammonia and mixed oxides of nitrogen are self-igniting at 160° F.

DISCUSSION OF RESULTS

All results reported herein were obtained with the use of quick-opening propellant valves; therefore any conclusions derived from them are strictly applicable only to similar rapid initiations of propellant flow.

Although engine starts attaining full steady-state combustion-chamber pressures were obtained in all runs at sea-level pressure regardless of type or presence of catalyst, the various means of ignition were not equally suitable in performance. Of the three methods, the use of lithium was the most desirable because it yielded consistently good starts in which the final steady-state combustion-chamber pressures were reached in the shortest period of time. In contrast with the lithium series, engine starts made with calcium as the catalyst and with no apparent catalyst were comparatively undesirable because they were erratic with respect to combustion-chamber pressure changes with time, they had pressure transients of much greater magnitude than the final steady-state values, and the times to attain maximum chamber pressure were usually considerably longer.

No definite explanation for the observed occurrence of two distinct pressures that were constant with time can be offered. It is not due to mechanical peculiarities inherent in the experimental apparatus since similar results were obtained during experiments with the same propellant

combination in another engine (ref. 1). Perhaps the two-step pressure-time curves are due to consecutive chemical reactions such as nitration followed by oxidation. Contribution of each of these reactions to a successful engine start may be depicted schematically as in figure 8(a). Another possibility is that flash distillation of the mixed oxides of nitrogen occurs as it enters the combustion chamber so that any significant reaction in the chamber involves only one of the oxides initially. Oxidation involving both oxides is delayed until the pressure and temp-
3184 erature have increased appreciably. This may be shown graphically as in figure 8(b). Still other explanations appear possible.

The simultaneous reduction of L^* and initial ambient pressure decreased combustion efficiency to a point where satisfactory engine operations were not obtained in runs with no added catalyst (runs 249 and 248, fig. 7). The shorter propellant stay-time in the smaller combustion chamber may have accounted in large part for these results. Although the reduced pressure may be another factor contributing to the unsuccessful engine starts, it is probably of lesser importance.

SUMMARY OF RESULTS

A study of the ignition of ammonia and mixed oxides of nitrogen at 160° F was made with and without fuel additives primarily at sea-level pressures utilizing a small-scale rocket engine of approximately 200-pounds thrust and a characteristic length L^* of 50 inches. In addition, some auxiliary experiments were conducted at pressure altitudes of 61,700 and 84,300 feet with a similar engine of 25 inch L^*. Oxidant-fuel ratios ranged from 1.9 to 3.0.

All 29 runs of this investigation conducted at sea-level pressure resulted in engine starts which were followed by stable combustion reactions and which yielded steady-state combustion-chamber pressures ranging from 238 to 452 pounds per square inch gage.

The use of lithium as a fuel-line additive was the most effective of the three starting means. It resulted in consistently good starts in which steady-state chamber pressures were attained in the shortest periods of time. Runs with either calcium as a fuel-line additive or with no additive generally required much longer time intervals to reach steady-state operating conditions, occasionally exhibited excessively high pressure pulses, and were usually more erratic with respect to variations of combustion-chamber pressure with time.

A successful ignition but an unsuccessful start was obtained with each of two runs conducted at subatmospheric pressures with no added catalyst.

CONCLUDING REMARKS

Although it has been shown that no ignition or starting difficulties will occur at sea-level pressure under the experimental conditions described herein, there are still some questions which remain unanswered by these results.

(1) It is not known whether aluminum in the form of chamber walls and fuel-line fittings acts as an ignition catalyst at 160° F. An answer to this question could be obtained with apparatus of stainless-steel components. 3184

(2) If it is shown that aluminum is not a catalyst, it may be concluded that ignition at 160° F is a thermal phenomenon. In that case, determination of the minimum thermal ignition temperature would be of definite value, especially in design applications.

(3) The effects of variations of propellant flow rates and programming on engine starting characteristics are not known. If this information were available, smooth starts without high pressure transients might be obtainable with catalysts other than lithium.

(4) Additional experiments with various fuel-line additives are needed to define the bounding limits of parameters such as characteristic chamber length, initial ambient pressure, and oxident-fuel ratio which must not be exceeded in order to maintain satisfactory engine starting and operation.

(5) It would be of value to determine the role of each component of mixed oxides of nitrogen in the ignition process.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, March 19, 1954

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2. Ladanyi, Dezso J., Sloop, John L., Humphrey, Jack C., and Morrell, Gerald: Starting of Rocket Engine at Conditions of Simulated Altitude Using Crude Monoethylaniline and Other Fuels with Mixed Acid. NACA RM E50D20, 1950.

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TABLE I. - SUMMARY OF DATA FOR ENGINE STARTING WITH ANHYDROUS AMMONIA AND MIXED OXIDES OF NITROGEN

[Successful ignition in all runs]

Run	Average propellant temperature, °F	Combustion-chamber pressure, lb/sq in. gage	Calculated total propellant flow, lb/sec	Calculated oxidant-fuel weight ratio
Lithium as catalyst (Sea-level pressure; 50-in. characteristic length)				
[a]214	160	437	0.99	2.04
215	160	452	1.07	2.01
[a]216	160	382	0.96	2.13
[a]218	163	367	0.93	2.36
[a]221	160	[b]305	0.95	2.15
222	161	[b]305	.97	2.60
[a]223	160	317	0.91	2.20
224	160	306	.91	2.44
225	159	308	.90	2.60
226	159	328	.85	3.04
[a]227	158	293	0.89	1.90
228	160	290	.89	2.14
229	160	280	.90	2.22
230	162	280	.89	2.46
231	161	274	.89	2.53
232	162	242	.73	2.32
Calcium as catalyst (Sea-level pressure; 50-in. characteristic length)				
[a]233	160	279	0.90	1.93
234	158	238	.91	1.95
[a]236	160	386	0.94	2.26
237	160	372	.98	2.95
238	160	(c)	(c)	(c)
[a]239	160	349	0.95	2.12
240	159	366	.98	2.98
241	159	380	.81	2.09
No apparent catalyst (Sea-level pressure; 50-in. characteristic length)				
[a]243	163	382	0.94	2.13
244	164	382	.95	2.53
245	165	382	.95	2.56
246	165	382	.95	2.64
247	164	[c]320	(c)	(c)
(Subatmospheric pressures; 25-in. characteristic length)				
[d]249	160	156	1.04	2.46
[a,e]248	160	160	1.04	2.22

[a]Initial run made with new propellant and catalyst load.
[b]Questionable accuracy because of instrument zero shift.
[c]Propellants depleted before attainment of steady-state pressure.
[d]Initial pressure altitude, 61,700 feet (50.0 mm Hg).
[e]Initial pressure altitude, 84,300 feet (17.0 mm Hg).

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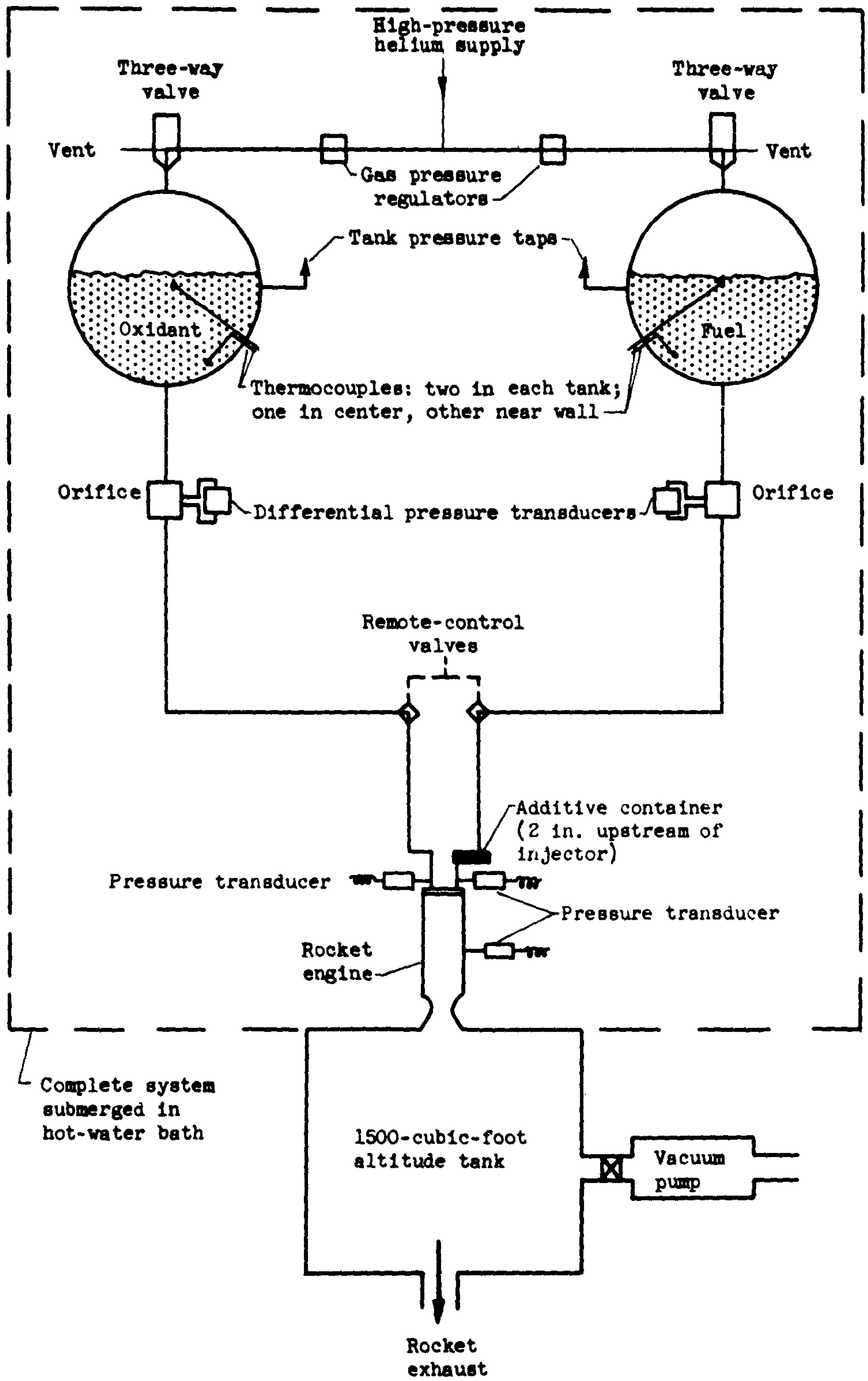

Figure 1. - Diagrammatic sketch of rocket-engine flow system for ignition experiments at 160° F.

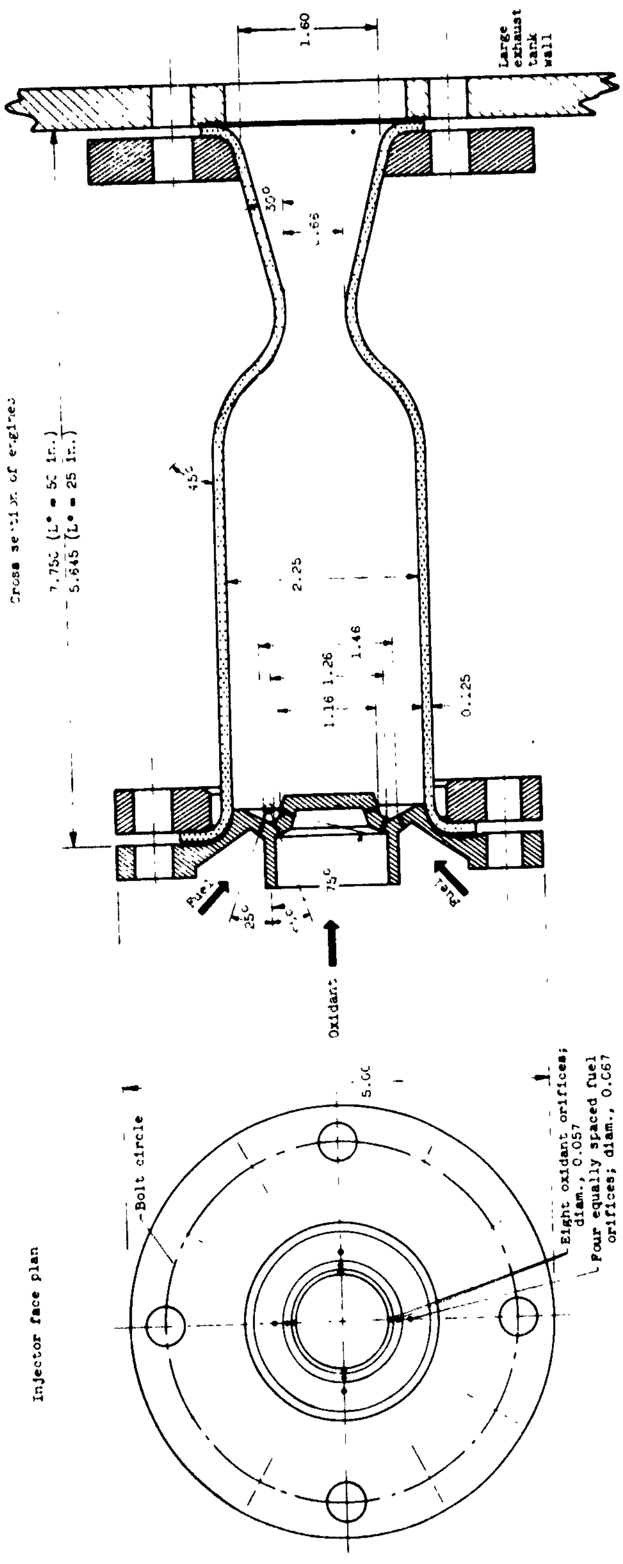

Figure 2. - Detailed views of 200-pound-thrust engines. (All dimensions are in inches.)

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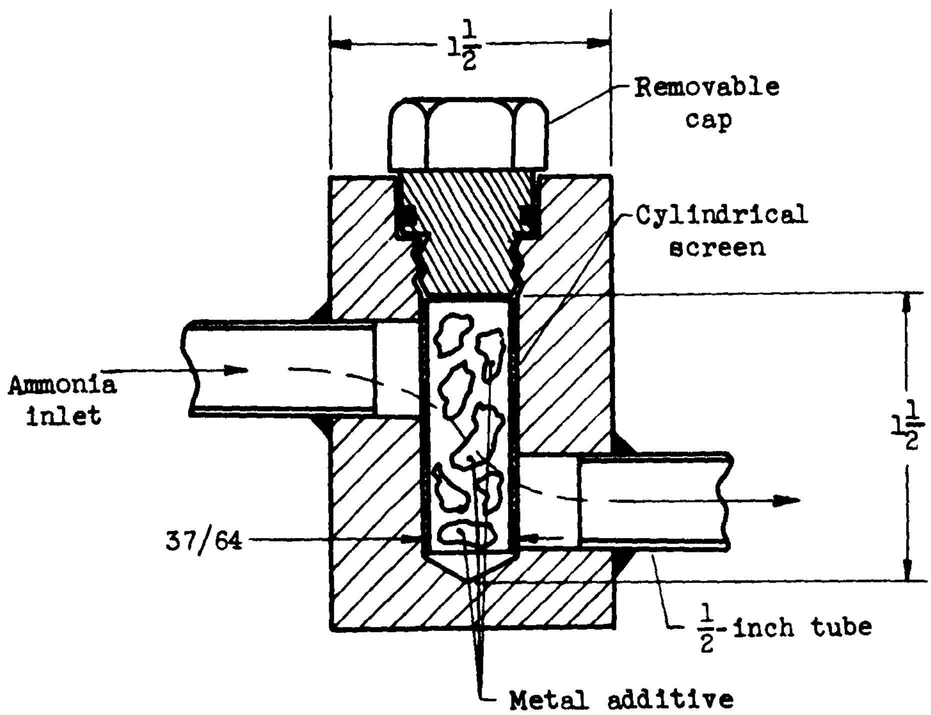

Figure 3. - Fuel-line catalyst receptacle.

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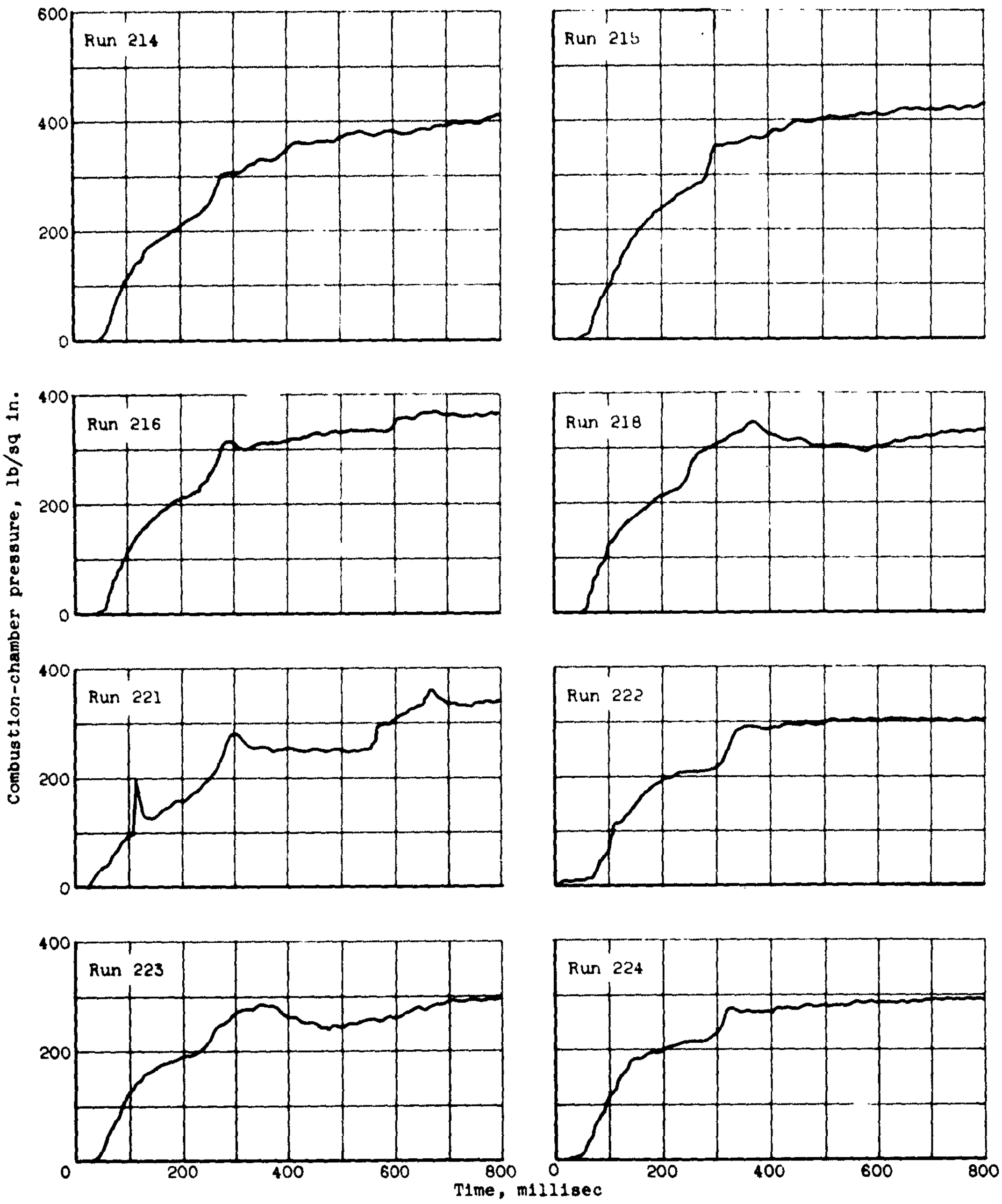

Figure 4. - Variation of chamber pressure with time for runs using lithium as ignition catalyst. Sea-level pressure; L* = 50 inches.

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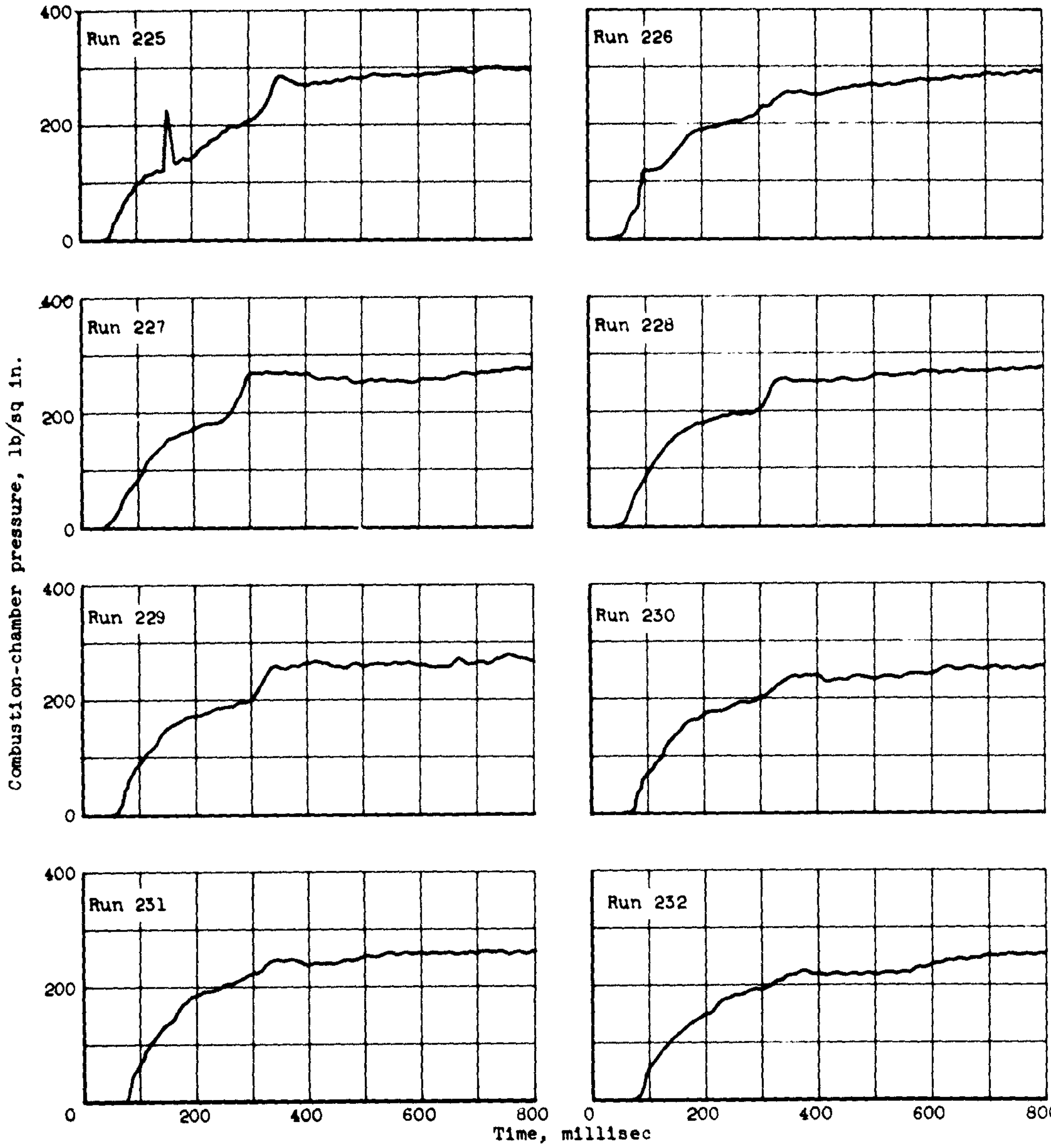

Figure 4. - Concluded. Variation of chamber pressure with time for runs using lithium as ignition catalyst. Sea-level pressure; L* = 50 inches.

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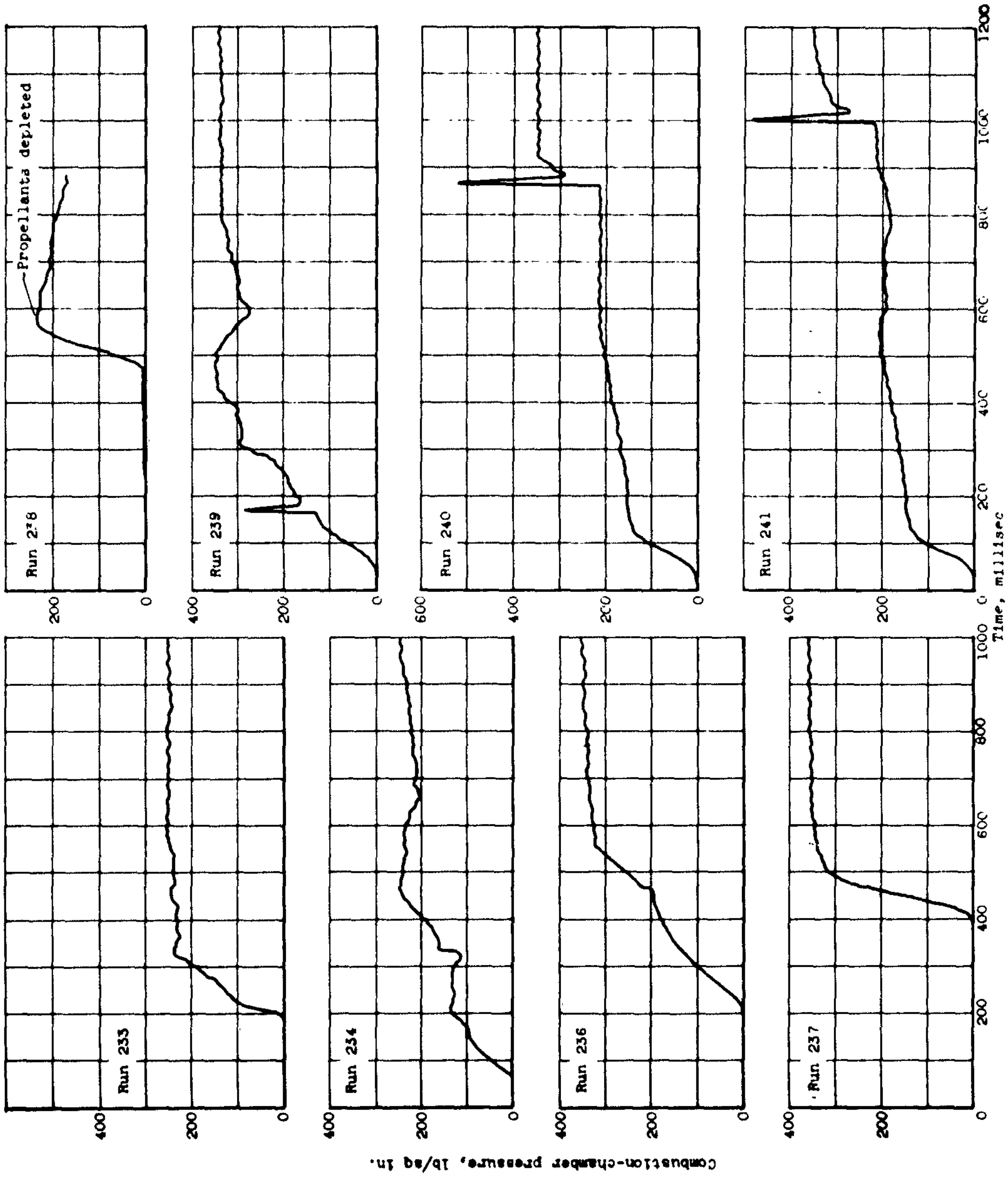

Figure 5. - Variation of chamber pressure with time for runs using calcium as ignition catalyst. Sea-level pressure; L* = 50 inches.

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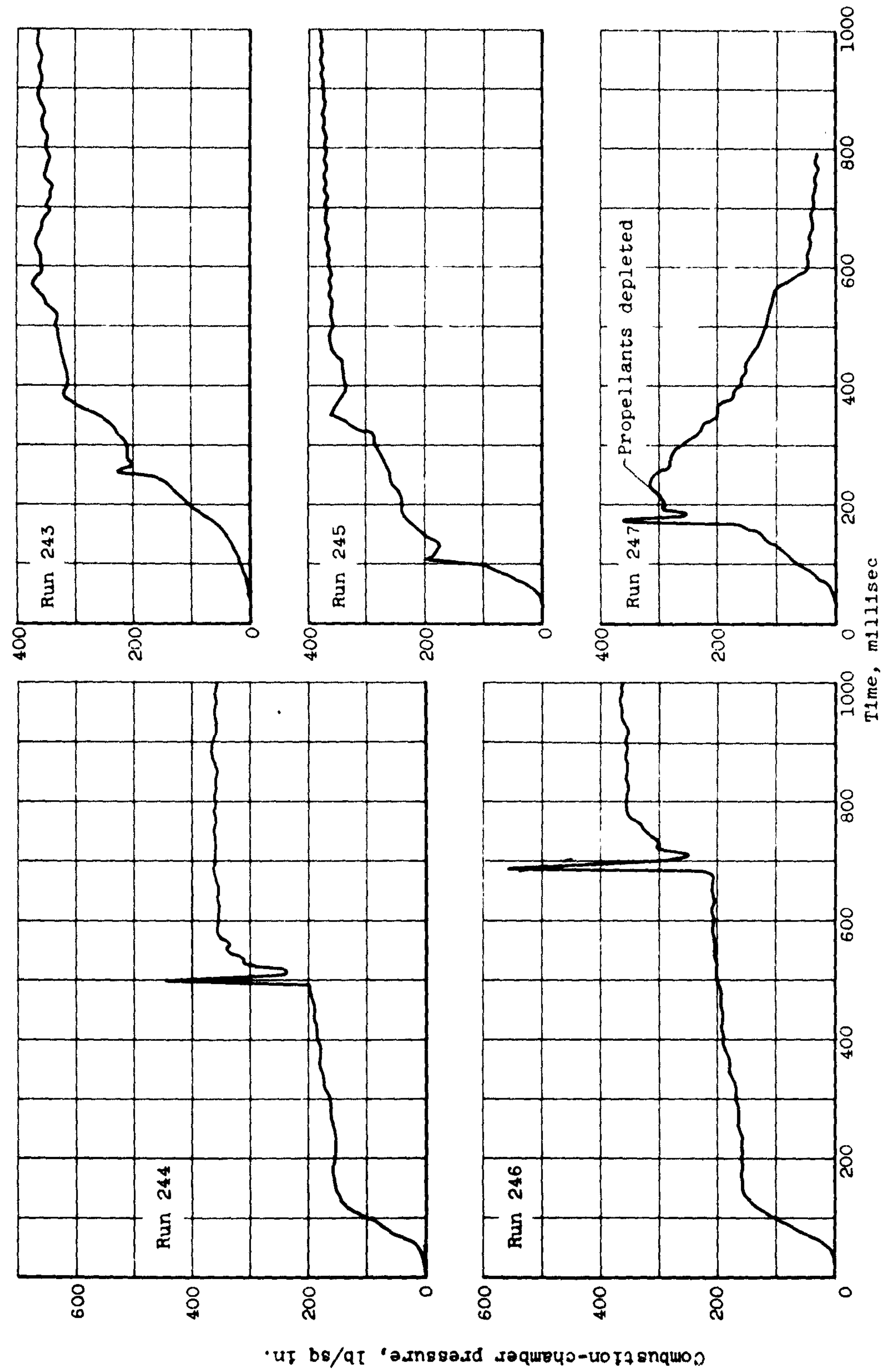

Figure 6. - Variation of chamber pressure with time for runs without added ignition catalyst at sea-level pressure. L* = 50 inches.

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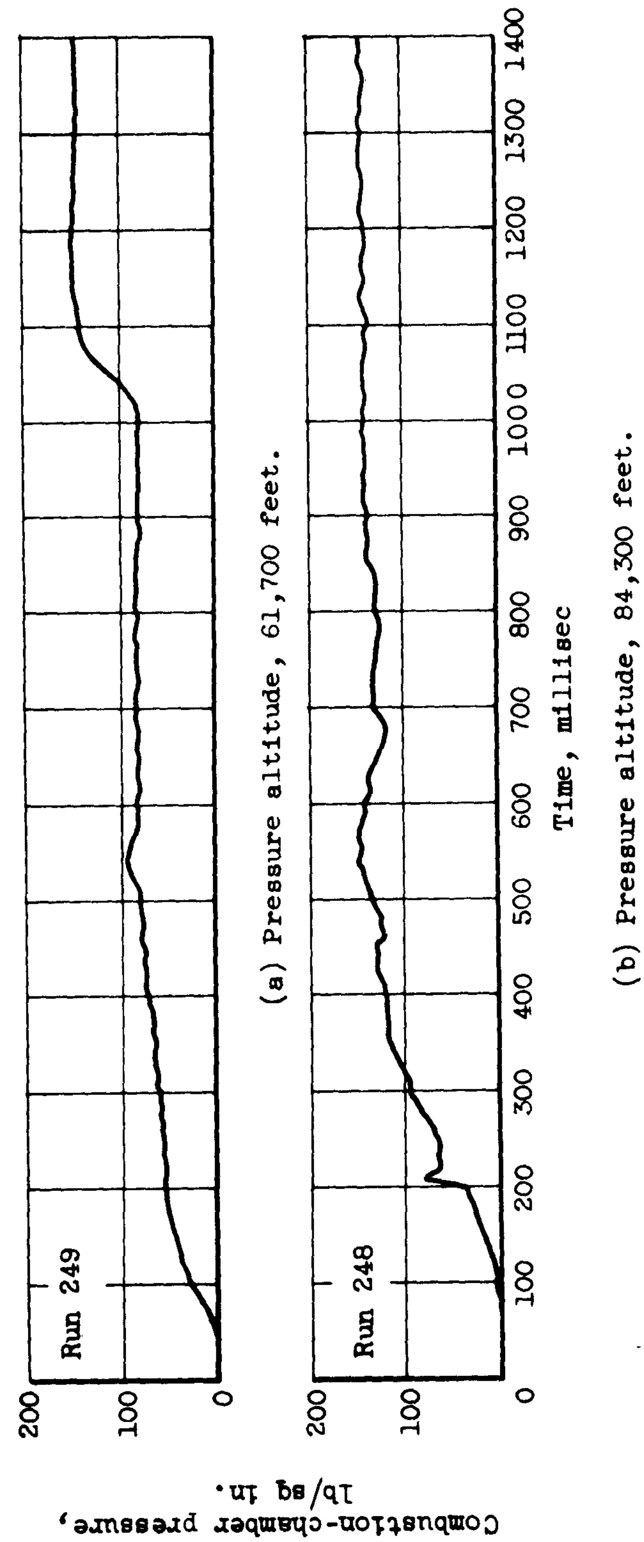

(a) Pressure altitude, 61,700 feet.

(b) Pressure altitude, 84,300 feet.

Figure 7. - Variation of chamber pressure with time for runs without added ignition catalyst at two pressure altitudes. L* = 25 inches.

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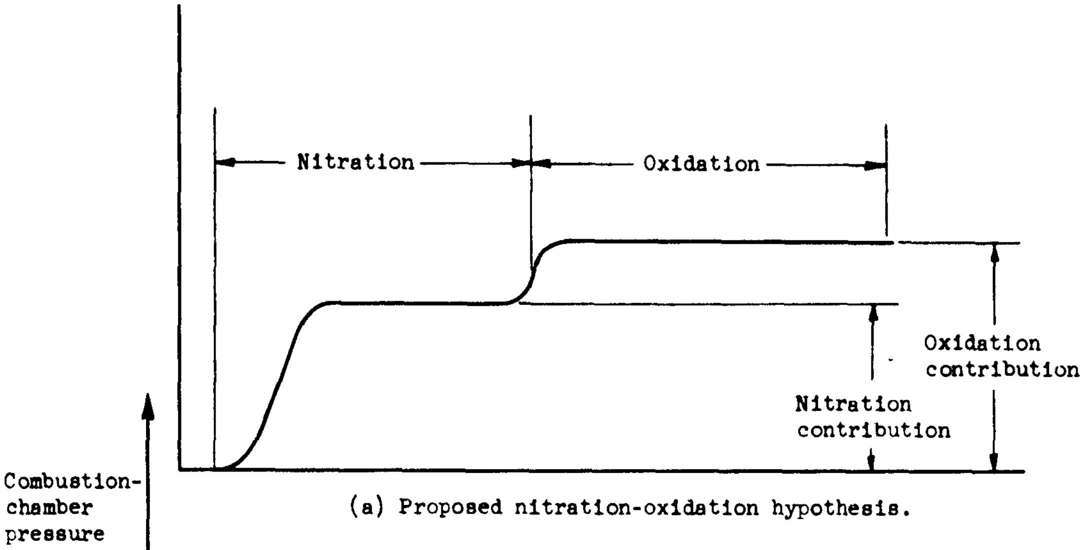
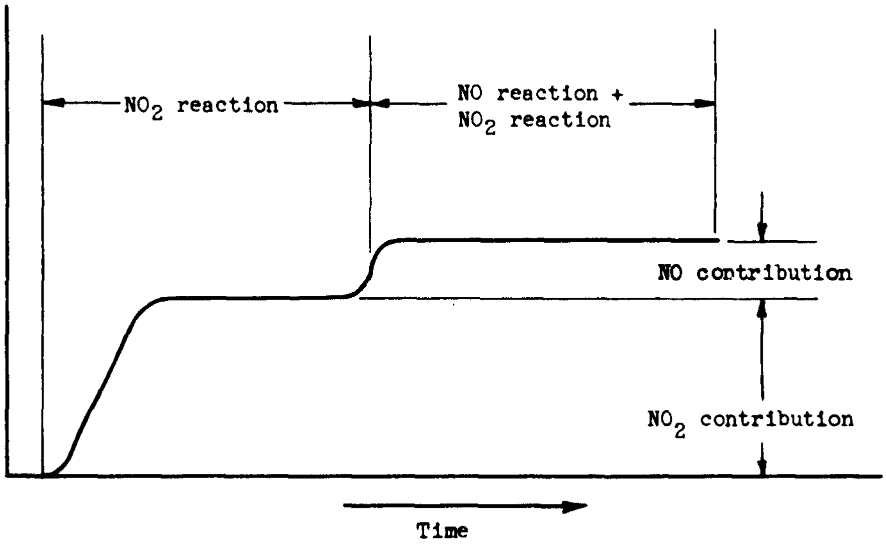


(a) Proposed nitration-oxidation hypothesis.



(b) Proposed NO_2 - NO hypothesis.

Figure 8. - Graphical representations of two hypotheses to explain combustion-chamber-pressure - time relations.

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